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CONDUCTING POLYMER MATERIALS

V. Ye. Gul

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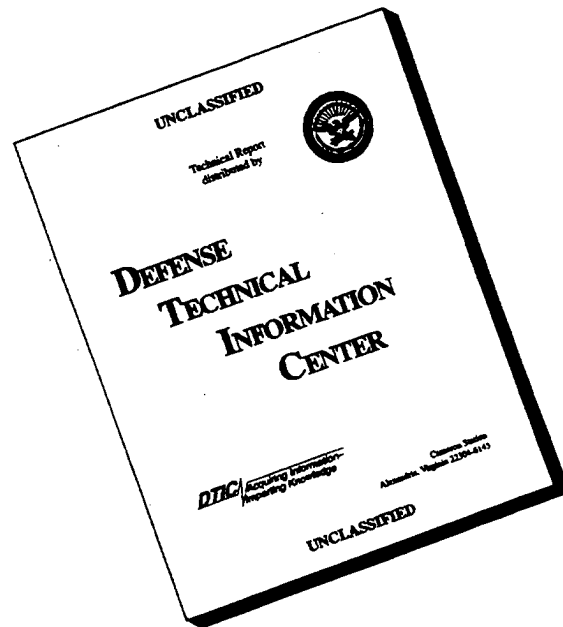PICATINNY ARSENAL, DOVER, N. J.

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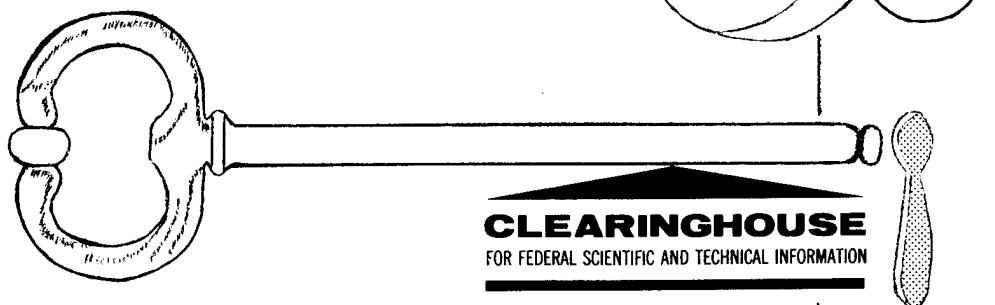
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JPRS 48359

7 July 1969

CONDUCTING POLYMER MATERIALS

BY

V. YE. GUL'

- USSR -

CONDUCTING POLYMER MATERIALS

- USSR -

In contrast to the metal conductors used at present, conducting polymer materials have the following advantages: high corrosion resistance, ease of workability when manufacturing products of complex shapes, lower specific weight, elasticity and bend resistance, the possibility of operation with multiple deformations, cheapness and great accessibility in comparison with metals. They can replace rare nonferrous and precious metals -- lead, copper, aluminum, silver and so on [1-6].

Several basic areas of utilization of conducting polymer materials, for example heating various media by an electric current, are known.

As examples of utilization of conducting polymer materials for heating purposes, let us mention the following: the manufacture of rubber or plastic heating elements for heating indoor facilities (Figures 1, 2) instead of steam radiators; heating work areas on oil drilling rigs and at open air installations of chemical plants; electrical heating of concrete and reinforced concrete structural elements; manufacture of heating stoves, and so on; manufacture of elastic electrodes used in medical practice for physiotherapy instead of lead, heating hothouse incubators and so on.

The development of such branches of the national economy as agriculture, machine-building, the aviation industry and also the development of railroad transportation with a simultaneous sharp increase in the power base have set the problem of development and creation of new materials by means of which it would be possible to insure accurate, safe thermostating of various units and systems and also heating accomodations and various devices with a high degree of reliability for appreciable time intervals.
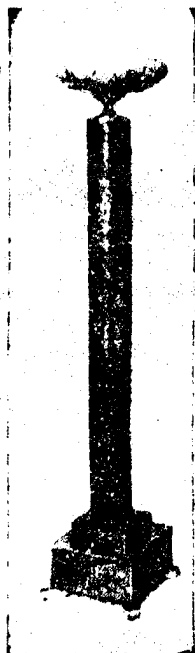
Figure 1. Illuminator--heater. This instrument was designed
for simultaneous heating and illuminating part of a residen-
tial or production accomodation . It is made of conducting
sheet polymer material with polymer decorative and insulating
covering.

The alloys and high resistance metals used earlier for electro-
thermostating could not insure operation of the systems in accordance
with the new requirements. This problem is most successfully solved by
utilizing electrical heating elements based on polymers.

Conducting polymer materials are also irreplaceable when removing
static electricity and grounding various objects. As specific examples
of using conducting polymer materials for purposes of removing generated
electricity, it is possible to mention the following: the manufacture of
rubber parts for anesthesia equipment and other instruments used in op-
erating rooms, the manufacture of nonelectrifiable conveyor belts for coal
mines and shops operating with the application of solvents where electrifi-
cation can cause a spark and fires and explosions as a result of this;
the manufacture of nonelectrifiable screening belts made of polymer ma-
terials as a substitute for metal (Figure 3, 4); nonelectrifiable air
ducts in coal mines which at present are a source of sparks and fires as a
result of friction of the air passing through them; the conducting covers
of balloons and dirigibles; nonelectrifiable coating of printing plates and
rolls in the polygraphic industry; the manufacture of conducting aviation
tires permitting grounding of the aircraft when parked and also the

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manufacture of conducting automobile tires for gasoline carriers and refuellers; the coating of the rolls of spinning looms in the textile industry; the manufacture of conducting rubber footwear and protective clothing for working under conditions of high-voltage current .

The utilization of conducting polymer materials for mounting parts in the electronic and instrument building industry is no less important.

Figure 2. Heating screen. Manufactured from the same material as the product in Figure 1.

Figure 3. Screening machine with drum made of a conducting polymer material preventing the grain from getting into the drum by electrification.

Conducting paints and enamels for the manufacture of film solar energy photoconverters are manufactured at present from conducting polymer materials. These materials are also used to obtain exact copies of metal products of complex shape by the galvanoplastic method (Figure 5,a, 5,b), for the manufacture of flexible screens and elastic sensors and diaphragms, and for the manufacture of transparent antistatic coatings.

Broad application of electronic equipment in all branches of the economy has forced domestic researchers (A. A. Berlin, V. A. Kargin, B. A. Krentsel', I. A. Ostryakov, Ya. M. Paushkin and others) to actively engage in finding cheap and low-deficit materials with semiconducting properties.

Depending on the purpose and area of application of the products various requirements are imposed on such materials. The main requirement is the capacity to conduct an electric current.

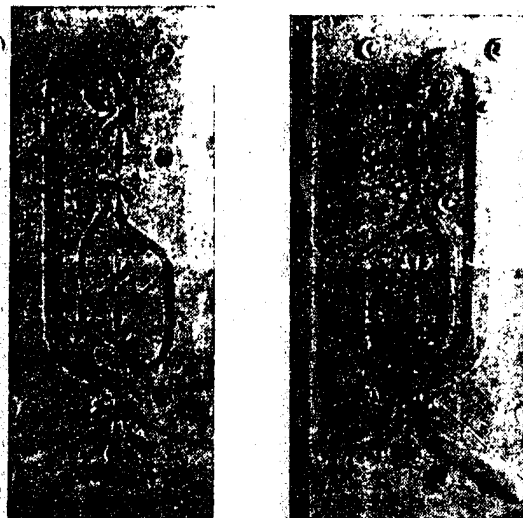Figure 4. Grain screen made of a conducting rubber.

Figure 5,a. Mold made of conducting plastic material.

Figure 5,b. Impression taken with a conducting antiadhesive mold made of polymer material.

In solutions, polar solvents and in salt melts and also in many solid substances, the passage of a current is accompanied by transfer of particles of the substance.

In metals an electric current is not accompanied by displacement of atoms of the substance itself: it is accompanied by electron motion. In accordance with quantum theory an electron can be in strictly defined states. On conversion of an electron from one quantum state to another, light of a strictly defined frequency is radiated or absorbed. Only one electron of an atom can be in each quantum state at a given point in time. If an

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electron in one of the possible states occurs in the system, then there cannot be another electron in the same quantum state in the same system.

Polymers, as a rule, consist of molecules the atoms of which have a complete outer layer of electrons and all possible quantum levels of the outer layer of electrons are filled. For example, if in carbon or silicon atoms making up the basic chain of micromolecules, four electrons of the outer (L-level) layer are coupled to two electrons of the nearest neighbors along the chain and to two electrons of substitute atoms, then all possible quantum levels of the outer layer of atoms making up the chain turn out to be filled with electrons. In such a solid state it is impossible to cause an electric current. An electric current could occur if electrons moving in the direction of the electric course acting on them in an electric field were accelerated, and the electrons moving in the opposite direction were decelerated. However, acceleration and deceleration amount to transition of the electrons to a new quantum state with higher or lower velocity. However, in the described polymers, in spite of the presence of a large number of electrons and the presence of an electric force, the state of motion of the electrons cannot change. In order that an electric current pass through the investigated polymer, the given state of the electron should be replaced by another characterized by a higher or lower speed than the given one. However, as a result of the fact that each of the possible quantum states of motion is "busy," both before applying the electric field and after its occurrence in the polymer there will be an identical number of electrons moving in one of the possible directions and opposite to it. Thus, the polymer behaves as an insulator. If the solid state consists of molecules or atoms the external electron layers of which are not filled with electrons, for example, in metals, then there will be fewer electrons in the outer electron layer of each atom than corresponding quantum states. For example, for single-valent metals in the outer electron layer of each atom there is one electron and more quantum states. If in such a solid state there are N atoms, then as a result of their interaction each quantum state of the electron is split into several different states. In each of these states there can only be one out of the N electrons. The electrons making up the solid state occupy N levels with the least energy. The remaining levels characterized by greater energy remain unoccupied. On applying an external electric field, the electron can accelerate its motion in the direction of the field, that is, it can make the transition to the new state with greater velocity if it is free of other electrons. This is possible since a larger number of free states is left in the solid state. In accordance with quantum theory, the electrons, the states of motion of which differ little from the quantum states not occupied by other electrons, should be considered free electrons.

We have investigated two types of materials: metals with free electrons and polymers with bound electrons. The former are good conductors of an electric current, and the latter are insulators. However,

polymer insulators also conduct current [7]. Whereas a voltage of 1 volt creates currents in 1 cm^3 of metal measurable in hundreds of thousands of amperes, in a polymer insulator under the same conditions the current strength is 10^{-12}–10^{-17} amps. The mechanism of conductivity of polymers is not known at present. The characteristic of the capacity of a sample to conduct current is resistance (or conductivity) calculated with consideration of the polarization emf [8].

The true conductivity of polymer insulators, as in all liquid and solid dielectrics, arises from the ocean of ions or electrons and therefore should depend on the concentration, mobility and charge of the carriers. The strength of the current passing at the time t through a sample of polymer should also depend on the displacement current arising as a result of variation in voltage in the sample and variation of its dielectric constant as a result of polarization.

Recently, a number of polymers have been detected which have the properties of semiconductors [9–22].

If we consider that in an individual atom, in addition to the normal electron states, excited states characterized by greater energy are also possible, then on conversion to the solid states each of the excited levels should also split into N individual levels. In a polymer semiconductor an electron can be converted (by heating) from the zone of normal states completely filled with electrons to the zone of excited states free of other electrons (a set of closely arranged energy levels is called a zone).

These electrons turn out to be among the unoccupied -- close to them -- quantum levels and can participate in the formation of an electric current. If the thermal motion is sufficiently intense, and the work of transition of an electron to the free state is small, the solid state becomes a conductor. Such solid states will be called semiconductors. With an increase in temperature a number of free electrons in the semiconductor should increase, while in metals the capacity of the electrons to participate in the passage of a current does not depend on the kinetic energy of the thermal motion. On the contrary, interference with the electron flux in metals increases with an increase in temperature.

In semiconductors, not only is motion of the free electrons possible but also a positive charge transfer. In accordance with quantum theory this is equivalent to displacement of the levels -- holes -- not occupied by electrons.

Polymers the conductivity of which increases with heating and illumination are called polymer semiconductors. In addition, the conductivity of polymer semiconductors should be caused by electrons or holes and not by ions. The values of the specific volumetric resistance of polymer

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semiconductors at room temperature lie in the interval characteristic for standard semiconductors, $\rho_V = 10^5-10^{13}$ ohms·cm. On the basis of this

latter fact, conducting polymer materials with disperse conducting fillers are frequently classified as semiconductors since with a known relation of components they are characterized by values of ρ_V lying within the above-indicated range. However, from the discussion above it is clear that this is an insufficient basis for classifying conducting polymer materials as conductors or semiconductors.

When studying conductivity, the question arises as to the nature of charge carriers. From this point of view the Hall radiation effect is of special interest.

Hall effects are observed only when the current is caused by motion of electrons or holes alone.

As a rule, chains of polymer semiconductors consist of alternating binary or tertiary bonds. These bonds can be formed between two carbon atoms > C = C<, carbon and nitrogen-C = N-, two nitrogen atoms-N = N-, and between the atoms of cyclic aromatic nuclei. These structures in-sure conjugation with respect to the macromolecular chain.

In benzene the π-electron shells of adjacent carbon atoms overlap, and a united electron system is formed. The necessary condition of conjugation of the electrons is that the axes of the π-electron shells be parallel.

In polyacetylene-C = C = C = C = C = C- all the σ-bonds are in one plane, and the π-bonds are perpendicular to it. The π-electron shells of the adjacent carbon atoms overlap.
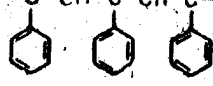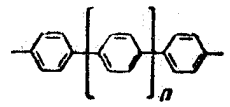
In polyphenylenes the aromatic nuclei are rotated by 33 degrees with respect to each other, as a result of which conjugation of the π-electrons between the phenyl nuclei is less than in the aromatic nuclei themselves.

On heating to 500-800 degrees C in the absence of air, organic compounds form systems of polycondensed nuclei without changing the initial form of the sample, for example, a fiber. This process is called graphitization. Materials formed by graphitization have low specific volumetric resistance -- from 10^{11} to 10^{-3} ohms·cm.

Table 1 contains the basic polymer semiconductors with a system of conjugated bonds.

As follows from what has been presented above, in polymers characterized by polyconjugation of binary or tertiary bonds, the π-electron

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Table 1

Characteristic of polymers with a conjugated system

(1) Структура цепей макромолекул	(2) Электропроводность при 20°C, ом⁻¹·см⁻¹	(3) Ширина запрещенной зоны, эв	(4) Число неспаренных электронов в 1 г полимера (ЭПР)
1	2	3	4
$-CH=CH-CH=CH-CH=$	$10^{-8}-10^{-12}$	0,4	10^{19}
$-C=CH-C=CH-C=CH-$ (три фенильных кольца)	$3\cdot10^{-19}$ $3\cdot10^{-18}$	2,2 1,4	10^{17} 10^{19}
$-C=CH-C=CH-C=CH-$ с R	10^{-10}	—	—
$-CH=CH-CH=CH-CH=CH-$ $-C\equiv C-C\equiv C-C\equiv C-$	10^{-6} 10^{-6}	—	10^{18} 10^{19}
$-C\equiv C-\langle \rangle-C\equiv C-$	$5\cdot10^{-11}$	0,86	10^{18}
$-C=N-C=N-C=N-$ с R	$10^{-5}-10^{-11}$	0,21—0,35	10^{18}
$-CH=CH-CH=CH-CH=N-$	$10^{-6}-10^{-11}$	—	—
$=CH-\langle \rangle-CH=N-\langle \rangle-N=$	$2,5\cdot10^{-11}$	1,06—2,4	10^{17}
$-C=N-N=C-R-C-$ с R	$1,1\cdot10^{-18}$ $7\cdot10^{-12}$ $1,29-10^{-14}$	1,2—2,1	$10^{17}-10^{18}$
$-\langle \rangle[\langle \rangle]_n\langle \rangle-$	10^{-19}	—	
$\{Ar-R\}_n\{Ar-N=N\}_m$ с R'	$10^{-11}-10^{-15}$	—	$10^{18}-10^{19}$

R=H, CH₃, COOH
R=—O—,—(CH₂)ₐ—,—CH=CH—

Key: 1. structure of the macromolecular chains
2. conductivity at 20°C, ohms⁻¹·cm⁻¹
3. width of the forbidden zone
4. number of unpaired electrons in 1 gram of polymer (EPR [electron paramagnetic resonance])
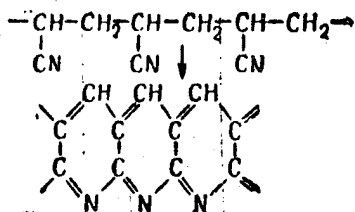
Table 1 continued

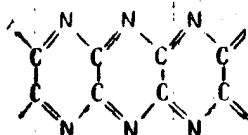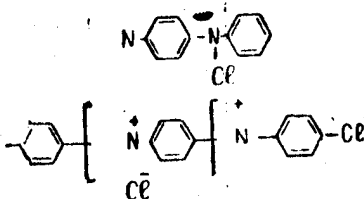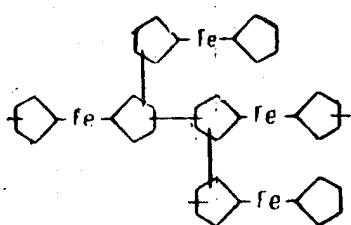| 1	2	3	4
(structure: polyacrylonitrile/pyrazine ladder polymer)	10^{-5}—10^{-8}	0,3—0,7	10^{19}—10^{20}
(structure: fused pyrazine/azine ladder)	10^{-5}	—	—
(structure: N,N'-diphenyl chloride / poly quaternary ammonium)	—	—	$4 \cdot 10^{18}$
(structure: ferrocene-linked multinuclear)	$6 \cdot 10^{-11}$	—	—
(structure: ferrocene carbonyl polymer)	10^{-7}	—	—

Table 1 continued

1	2	3	4
$\left[C = CH - CH = CH \right]_x$ (with phenyl substituent)	10^{-12}	0,27	$1 \cdot 10^{12}$
$\left[CH = CH - \overset{Br}{C} = \overset{Br}{C} \right]_n$	$1 \cdot 10^{-1}$ — $1 \cdot 10^{-2}$	—	—
$\left[\right]_x$ (phenol ring, OH)	$3 \cdot 10^{-6}$	0,47	$1 \cdot 10^{12}$
$-C \equiv N$ / CH / CH / $-C \equiv N$	$1 \cdot 10^{-4}$	0,012	$3,5 \cdot 10^{10}$
$-\overset{OH}{C} \equiv N$	—	—	$1 \cdot 10^{10}$
$-HC = CH - CH = CH -$ / $-C \equiv N-$	$1 \cdot 10^{-9}$	0,9	—
$\left[CH = CH \right]_x$ (ferrocene, Fe)	—	—	—

Table 1 continued

1	2	3	4
	$6 \cdot 10^{-6}$	—	—
	$6 \cdot 10^{-6}$	—	—
	10^{-8}—10^{-12}	$0{,}3$—$0{,}8$	10^{19}—10^{21}

shells of adjacent atoms overlap forming a united system of delocalized
π-electrons. These electrons are capable of carrying an electric current
within the limits of the macromolecular circuit. As a result of the fact
that the number of π-electrons does not depend on the temperature, the
electrical conductivity mechanism within the limits of the macromolecular
circuit of polymer materials should correspond to the mechanism of conduc-
tivity of metals. In order that the electric current pass through the
entire mass of substance, electron transitions between adjacent macro-
molecules are required. The potential barrier of the intermolecular inter-
action is overcome as a result of the kinetic energy of thermal motion;
therefore, the conductivity of these polymer semiconductors depends on
the temperature.

In a polymer semiconductor, the electron donors are not the indi-
vidual atoms of molecules but the macromolecules the mass of which is
several orders higher than that of atoms or molecules of inorganic semi-
conductors. Nevertheless, there is much in common in the properties of
inorganic and polymer semiconductors. The conductivity of semiconducting
polymers is within the same limits $\sigma_V = 10^{+2} - 10^{-11}$ ohms$^{-1} \cdot$cm^{-1} as that
of ordinary inorganic semiconductors. Their conductivity increases with
temperature by an exponential law just as for inorganic semiconductors
$\sigma_T = \sigma_0 e^{E/kT}$. The activation energy E (the width of the forbidden zone)
is on the order of 10.1-1.5 kcal/mole. Some polymer semiconductors are
capable of rectifying an electric current. This indicates the nonohmic
behavior at the contacts (n-p-junction). The occurrence of thermal emf's
within the limits of 3 to 300 millivolts/deg is characteristic of
polymer semiconductors just as for inorganic semiconductors. The concen-
tration of the current carriers in polymer inorganic semiconductors in
the conductivity zone with an increase in temperature increases strongly
at the same time as it does not change in metals. In contrast to ordin-
ary polymers, polymer semiconductors are paramagnetic as a result of
which magnetic susceptibility is observed in the polymer semiconductors.
The permeability of polymer conductors is >1 (for ferromagnetic solid
states the permeability is >>1, and for diamagnetic polymers, <1).

On the basis of the facts listed above, modified zone theory was
applied to polymer semiconductors. In accordance with the concepts of
this theory, π-electrons from compounds of an aromatic nature form a
semifilled zone or energy band with small distances between the energy
levels. The distance between the levels is also determined by the orbital
overlapping. As a result of this the aromatic compounds are superconduct-
ing along the conjugation circuit. In the case of polymers with polycon-
jugated bonds, two cases of conductivity are distinguished. The first
case is where the macromolecular zone is half filled. In this case the
mechanism of conductivity will occur just as for metals. The second case
corresponds to total filling of the zone. Then the conductivity mechanism

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corresponds to that for semiconductors.

When forming a solid state the adjacent atoms can come so near that their outer electron shells begin to overlap. On approaching to a distance of less than 10^{-7} cm there is orbital overlapping of adjacent atoms and molecules. This gives rise to the possibility of activationless electron transitions from molecule to another -- the tunnel effect. It is reasonable that this transition cannot generate an electric current if the macromolecule does not have mobile electrons which can shift along it. However, in semiconductor polymers with a system of polyconjugated bonds there are mobile π-electrons which are carriers of an electric current in the macromolecule circuit. The electric current between the semiconductor macromolecules flows as a result of exchange electrons. With an increase in the molecular weight the number of exchange electrons will increase. This is promoted by the presence of mobile π-electrons and the ordered arrangement of the chains of macromolecules in the packets and crystal lattice. The exponential dependence of the conductivity on temperature in polymer semiconductors can be determined by the concentration of exchange electrons (the number of π-electrons of the semiconjugation chain is constant).

An analogy between the mechanisms occurs in polymer semiconductors and metal-filled polymers. On the basis of analysis of the experimental data the impression is that within the limits of certain temperature values in the case of plastics filled with a conducting filler, the mechanism of conductivity characteristic of metals occurs. For sufficiently strict judgment of the nature of the current carriers, V. Ye. Gul' and V. P. Sokolova investigated plastic on the basis of epoxy resin with graphite and an admixture of kaolin. In plastic not subjected to heat treatment, the conductivity mechanism turned out to be characteristic of semiconductors (p-type) both inside the sample and on its surface. As for the samples subjected to heat treatment both in a vacuum and in the air, p-type conductivity with respect to the surface of the sample and n-type (electron conductivity) inside are characteristic of them. Gradually grinding off the surface and in this way controlling the nature of the conductivity, the authors established that the p-type conductivity is extended to a sample depth of 400-500 microns. In order to determine the Hall effect, the samples were made in such a way that p-type conductivity is observed in one sample on one side, and n-type conductivity on the other. In addition, samples with only p- or n-type conductivity on both sides were also manufactured.

The results obtained are presented in Table 2.

Thus, the problem of creating polymer materials combining specifically useful properties of polymers and conductivity inherent in conductors and semiconductors appears to consist of three parts.

Table 2

Type of sample	Concentration of current carriers, N/cm^3	Mobility in cm, cm/sec	Hall constant	ρ, ohms·cm
Nonheat treated, with 22% content of graphite; p-type	2.10^{17}	11.0	32	4.3
Heat treated with 22% content of graphite; p-type	3.10^{18}	12.0	4.9	0.4
Nonheat treated with 10% content of graphite; p-type	9.10^{15}	3.9	1406	280
Heat treated with 10% content of graphite; n-type p-type	$4.5 \cdot 10^{16}$ 5.10^{17}	3.0 0.2	157 12	51 56
Heat treated in a vacuum with 10% content of graphite: n-type p-type	6.10^{16} $1.1 \cdot 10^{17}$	3.5 1.0	140 57	39 57

First, it is necessary to sufficiently completely study the mechanism of conductivity of the polymers themselves and its relation to their structure.

Secondly, it is necessary to investigate the laws defining the dependence of ρ_V on the composition of the material, the nature of the fillers, the method of their dispersion, the dimensions and shape of the particles and also the structures and nature of the fillers formed in the system.

Thirdly, we should analyze what features of the chemical structure of the supermolecular structures formed in a conducting polymer material are responsible for one property or another; for example, strength, deformability, chemical stability and so on.

The problem of the mechanism of conductivity of filled conducting polymers is important since understanding of it offers the possibility of controlling the factors determining the conductivity of these

materials. Inasmuch as carbon black-filled conducting rubbers are the most studied, it is entirely natural that they served as the first objects of investigation.

Carbon black-filled rubbers begin to conduct current to a sufficient extent only for a certain concentration of carbon black [23]. One of the essential factors determining their conductivity is the nature of distribution of the filler in the system. It is natural to assume that the passage of the electric current in carbon black-filled systems is realized as a result of contacts between individual particles of carbon black, in other words, as a result of carbon black-carbon black couplings. However, there are different points of view regarding this question.

It is considered that direct contact between the carbon black particles exists with the formation of continuous carbon black lattices [23]. It is also stated that the contact between the carbon black particles is made by means of a thin polymer film through which emission of electrons is possible [24].

The basis for the first prerequisite was formed from studies of the nature and properties of carbon black. In these studies it is noted that some types of carbon black (particularly acetylene, anthracene, and so on) have the capacity of forming a developed chain or lattice structure. This is indicated by the electron microscopy data. It is explained by the fact that the surface of the particles of such carbon black has sections with increased adsorption energy. For example, measuring the differential heats of adsorption of various substances showed that there are sections on the surface of active carbon black used as fillers where adsorption occurs first of all and with the greatest thermal effect (15-20 kcal/mole) [25]. The existence of these free forces on the surface of the particles is caused by the difference in degree of packing density [26] and by the fact that the atoms in the layers are not in a state corresponding to the minimum energy.

The active sections on the surface of the carbon black particles can be represented as points at which the ends of parallel-end groups formed by graphite plates come to the surface. The possibility of existence of such points follows from the characteristic features of the crystal structure of active carbon blacks which was investigated in detail by studying the scattering of x-rays at low angles [27]. As a result of the known nonsaturation of the boundary atoms of carbon, the ends and angles of the crystals have increased energy.

B. A. Dogadkin with his co-workers [23] proposed that these carbon black structures are also formed during dispersion of carbon black in a polymer with a certain carbon black concentration. Here the system should be considered as a set of two continuous phases: rubber and carbon black.

This proposition is confirmed by calculating the average distances between the carbon black particles with a given concentration. They turn out to be equal to 100-180 A and significantly greater than the distance between the particles obtained by Ya. I. Frenkel' beginning with the observed conductivity.

Thus, in mixtures with   observed conductivity on the order of 10^{-2}-10^{-4} ohms^{-1}cm^{-1}, there is significant nearing of the carbon black particles by comparison with the averaged calculated distance. If the nearing of the carbon black particles leads to a direct contact between them with the formation of chain structures, then a linear relation is observed between the current strength and the applied voltage; that is, Ohms laws is observed. If the nearing of the carbon black particles does not end with direct contact of them, and the electric current is passed through an interlayer of polymer, the relation between the current strength and the voltage should not be linear, and the exponent n should appear in the equation:

$$J = CV^n.$$ (1)

The greater the proportion of particles separated by the rubber interlayer, that is, the greater the proportion of couplings of the carbon black-rubber type, the greater the exponent n.
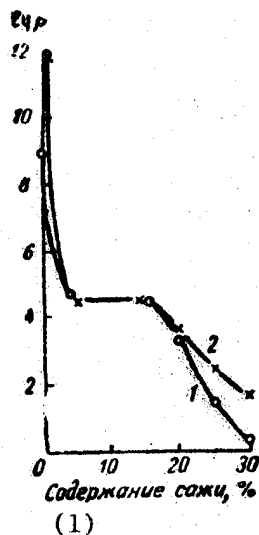

(1)

Figure 6. Variation of the speicific volumetric conductivity of phenolformaldehyde (1) and epoxy (2) compositions depending on the carbon black content

Key: 1. carbon black content, %

Table 3

Carbon black	n
Channel black	1.26
Anthracene black	1.18
Furnace black	1.88
Jet black	2.73
Lamp black	2.77

Equation (1) is valid for all the investigated rubbers containing various carbon blacks. This is indicated by the fact that for all types of carbon blacks the relation $j = f(V)$ in logarithmic coordinates is linear.

In Table 3 we have the variation of the electrical characteristics as a function of the type of carbon black in the rubbers manufactured from bar sodium butadiene rubber.

From the data presented in Table 3 it follows that the most developed carbon black structures with predominance of the carbon black-carbon black bond ($n \sim 1$) form channel and anthracene black, and jet black ($n \sim 3$) forms the most developed structures with a small proportion of bonds of the given type. It is important to note that the listed carbon blacks are also arranged in the same order with respect to degree of their reinforcement of the rubber.

In the papers by V. Ye. Gul' with his co-workers [28, 29], it was demonstrated that the presence of chain structures is a necessary condition of good conductivity not only when filling rubber with certain types of carbon black, but also in the case of thermally reactive resins filled with carbon blacks. As an example, let us consider the results of investigating the structures of compositions consisting of phenol-formaldehyde resin of the resol type and epoxy resin E-40 with a different content of acetylene carbon black.

When investigating the unreinforced resins it turned out that their conductivity depends on the amount of carbon black introduced. First the increase in carbon black content has no essential effect on the conductivity. On reaching a carbon black concentration of approximately 30 percent, a discontinuous decrease in specific resistance is observed (see curve 1 in Figure 6).
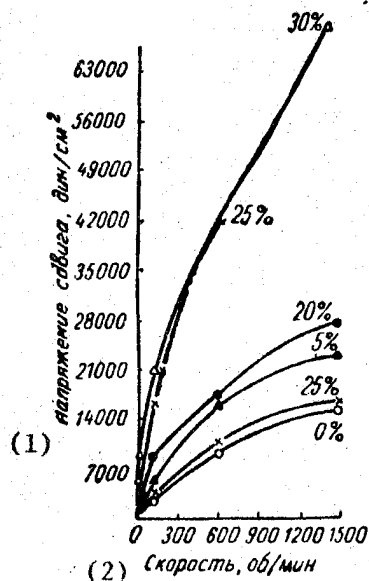
Figure 7. Variation in shearing stress of a suspension of carbon black in a solution of phenolformaldehyde resin with the strain rate. The numbers on the curves corresponds to the carbon black content.
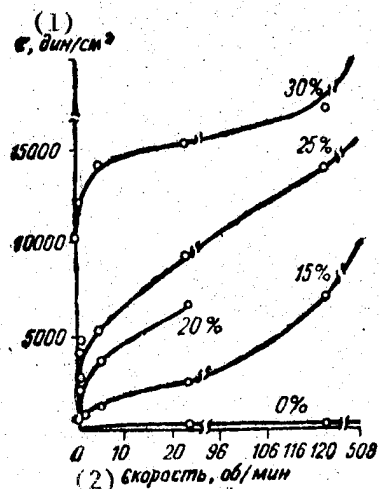
Figure 8. Variation in shearing stress of a carbon black suspension in an epoxy resin solution as a function of the strain rate. The numbers on the curves correspond to the carbon black content.

Key: 1. shearing stress, dynes/cm^2
2. speed, rev/min

Key: 1. dynes/cm^2
2. speed, rev/min

From the results of investigating the structural and mechanical properties of unconsolidated compositions presented in Figures 7 and 8 it follows that the shearing stress τ with an increase in strain rate increases smoothly in the case of unfilled phenolformaldehyde resins, approaching a value practically independent of it. This value depends strongly on the degree of filling with carbon black and, consequently, determines the strength of the structure formed by the carbon black particles. The investigated stress is appreciably greater in the case of carbon black compositions on the basis of phenolformaldehyde resins than in the case of analogous compositions on the basis of epoxy resins. Consequently, carbon black particles will form a stronger structure in compositions based on formaldehyde resin.

Electron microscopic investigations of unconsolidated compositions of phenolformaldehyde resin have confirmed that the addition of carbon black to the resin does not lead simply to an increase in the amount of carbon black in the resin but also to a qualitative change in the resin structure. The same is also observed during electron microscopic investigation of consolidated compositions.
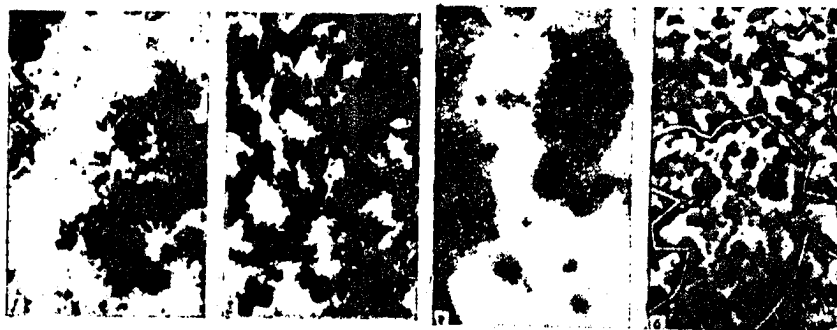
Figure 9. Electron microphotographs of compositions on the
basis of the furfurolacetone monomer (1,2) and on the basis
of phenolformaldehyde resin (4,3): 1 -- unconsolidated compo-
sition with 50% carbon black; 2 -- 4 -- consolidated compo-
sition with 40, 20 and 30% carbon black.

In Figure 9 it is obvious that with a carbon black composition up
to 30%, it is distributed in the form of individual, unconnected particles
the amount and size of which increases proportionally to the increase in
concentration of the carbon black introduced, that is, before a certain
concentration of carbon black, the resin is the disperse phase in which
particles of the filler are distributed (Figures 1 and 3). With a con-
centration of 30 percent, there is a qualitative change in the structure.
The particles of carbon black touch, forming chain structures which can give
a single three-dimensional lattice which obviously is the cause of a sharp
decrease in the electrical resistance (Figure 2, 4).

The cause of the better conductivity of compositions based on phenol
formaldehyde resin by comparison with the conductivity of compositions based
on epoxy resin with the same content of carbon black obviously is the chemi-
cal nature of the resins themselves. The electron microscopic studies of
unconsolidated compositions showed that in the case of phenolformaldehyde
resin, the carbon black is distributed in the mixture in the form of parti-
cles having a larger specific surface. This is expressed in the fact that
the carbon black particles do not have a sharp interface as a result of the
fact that they are surrounded by a large number of fine particles of carbon
black; the size of many of these particles is less than the resolution of
the microscope (25 Å). This is not observed in the case of epoxy resin.
Here the resin-carbon black interface is expressed sharply, and there are
appreciably fewer fine particles of carbon black than in the phenolformal-
dehyde composition.

In the case of an epoxy resin, the particles try to have a minimum
specific surface. This indicates the better combinability of the phenol-
formaldehyde resin with the carbon black. A confirmation of this situation
is the effort of the carbon black and epoxy resin to separate during the
process of evaporation of the solvent from a film applied on a slide.
This effort to separate is not observed in the case of phenolformaldehyde
resin.

In the case of phenolformaldehyde composition we have a uniform mixture of resin and carbon black, and in the case of epoxy, there is a clearly expressed stratification of the two components: epoxy resins with a small amount of carbon black and carbon black with a small admixture of resin. Thus, electron microscopic investigations of the unconsolidated carbon black filled compositions have clearly established that the chemical nature of the binding polymer has an essential effect on the conductivity of the compositions. Poor combinability of the epoxy resin E-40 with acetylene carbon blacks promotes the formation of large aggregates of carbon black with smooth outlines, and it is an obstacle to the occurrence of the chain structures.

The structural changes occurring during the process of consolidation of the compositions based on phenolformaldehyde resin of the resol type and epoxy resin E-40 with a different content of acetylene carbon black were traced, and the results obtained were compared with the results of measuring the electrical properties (see Figures 6,a and 6,b in which curves are presented for the variation of the specific resistance of phenolformaldehyde and epoxy resins with a different content of acetylene carbon black as a function of the consolidation time).

The results obtained indicate that the consolidation process has an essential effect on the conductivity of the composition. The fact that the specific electrical resistance of the mixtures drops with heat treatment indicates that the mechanism of heat treatment is the same in both cases. It can be connected both with variation in concentration of the carbon black as a result of a decrease in the volume of the system during consolidation and with variation (most probably, with dispersion) in the structures formed by the carbon black particles occurring as a result of transverse cross-linking of the chain molecules.

The fact that the conductivity of the compositions is exhibited beginning with certain values of the carbon black concentrations attracts attention: if the carbon black concentration is close to this limiting value, increasing the actual carbon black concentration, for example, as a result of a decrease in the total volume during consolidation should lead to an essential decrease in the values of ρ_V.

From the data presented in Figures 10,a and 10,b it is obvious that the specific resistance of the compositions based on epoxy resin E-40 is higher than the specific resistance of phenonformaldehyde compositions: here the maximum variation of the specific resistance during the consolidation process is greater the greater the carbon black concentration is.

The fact that the value of the specific resistances of the unfilled resins differs by several orders from the corresponding values for compositions containing acetylene resin and also that an increase in the percentage content of carbon black is accompanied by a decrease in

the resistance indicates the defining role of the indicated type of
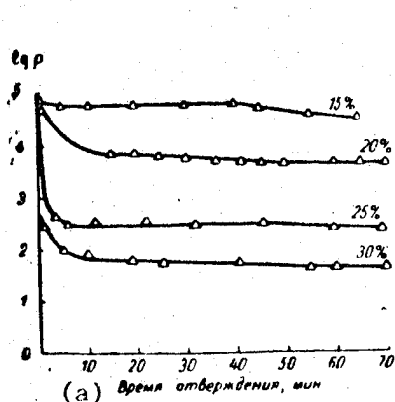carbon black in the conductivity of such systems.

(a) Время отверждения, мин

(a) Время отверждения, мин

Figure 10,a. The specific resistance
of epoxy compositions as a function
of consolidation time. The numbers
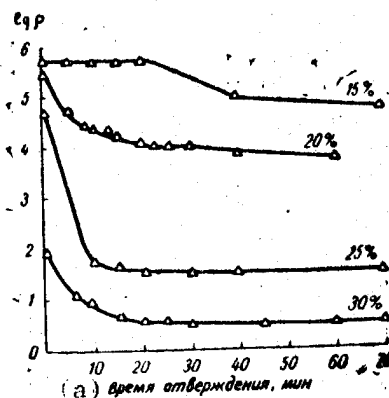on the curves correspond to the car-
bon black content

Figure 10,b. The specific re-
sistance of phenolformaldahyde
compositions as a function of
consolidation time. The numbers
on the curves correspond to the
carbon black content.

Key: a. consolidation time, minutes

However, the difference in the values of the conductivity of the
consolidated systems based on phenolformaldahyde resin from the values
of the conductivity of epoxy compositions is another confirmation of the
essential role of the chemical nature of the binder. In the given case
obviously better combinability of the phenolformaldehyde resin with car-
bon black has significance. The statement by the authors regarding the
dispersion of the structures formed by the carbon black particles during
the consolidation process and the resultant increase in conductivity of
the system are confirmed by the structural-mechanical and electron micro-
scopic investigations of the compositions.

In Figures 11a and 11b we have the variations in shearing stress
with time of consolidation of the compositions based on phenolformalde-
hyde and epoxy resins with a different carbon black content. From com-
parison of these figures it is obvious that the effect of the degree of
filling of the polymer with carbon black on the process of consolidation
of the compositions based on phenolformaldehyde resins is different from.
that for the compositions based on epoxy resin. Increasing the degree
of filling of the first composition is accompanied by an increase in its
consolidation rate. The reverse picture is observed for the second
composition. It should be noted that not only does the consolidation
rate of the epoxy resin decrease with an increase in the carbon black
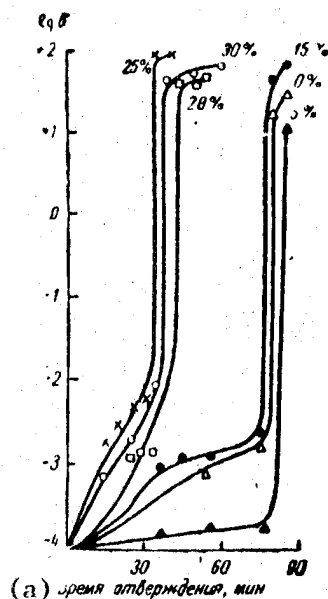content but also that the consolidation time of the epoxy compositions

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Figure 11a. Variation in shearing stress of phenolformaldehyde compositions with consolidation time. The numbers on the curves correspond to the carbon black content.
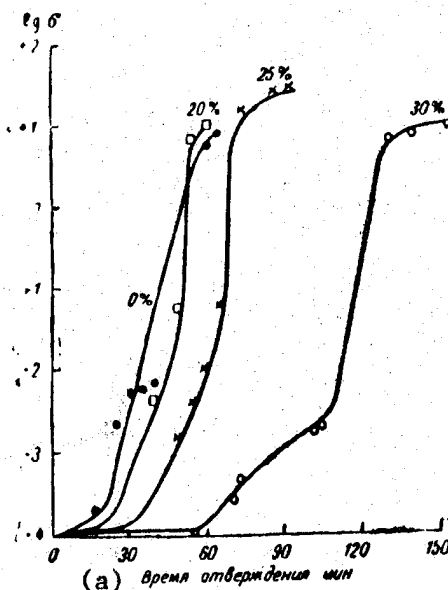
Figure 11b. Variation in shearing stress of epoxy compositions with consolidation time. The numbers on the curves correspond to the carbon black content.

Key: a. consolidation time, minutes

appreciably exceeds the consolidation time of the phenolformaldehyde polymer materials.

The higher rate of development of the three-dimensional structure in the case of phenolformaldehyde resin obviously promotes additional dispersion of the acetylene carbon black, an increase in the actual "partial" concentration of the latter and the formation of the current-conducting structures with smaller degrees of filling by weight.

In order to obtain additional information with respect to the mechanism of conductivity of such systems the form of the dependence of the current strength on voltage was determined for the consolidated compositions with clearly expressed chains of carbon black structures.

In Figure 12 we have the relation for compositions based on furfurolacetone monomer with a different carbon black content. Consolidation of all these compositions occurred at a temperature of 80 degrees C. At lower consolidation temperatures deviations from the linear
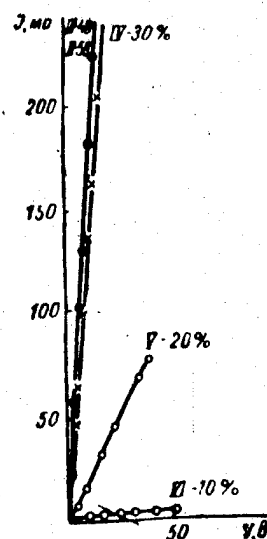
Figure 12. Volt-ampere characteristic of compositions based on furfurolacetone monomer. The numbers on the curves correspond to the carbon black content.

relation of current strength and voltage were observed. This deviation occurred for sufficiently large values of the current strength and voltage. It was obviously caused by local heating in the system as a result of Joule heat and the process of shrinkage and disturbance of the current-conducting chains connected with this.

When studying the temperature dependence of the specific resistance the temperature resistance coefficient for systems with chain carbon black structures was always positive up to a certain value of the temperature.

A further increase in temperature is accompanied by volumetric shrinkage of the material so significant that the number of carbon black-carbon black contacts increases and the specific resistance begins to decrease. With repeated heating and cooling cycles the temperature interval corresponding to positive values of the resistance coefficient increases.

In Figure 13 we have the resistance of the composition based on furfurolacetone monomer as a function of temperature.

If the above formulated concepts are valid, the consolidation at higher temperature should decrease the volumetric shrinkage occurring during the tests below this temperature and, consequently, decrease the

drop in resistance at sufficiently high temperatures. This was confirmed experimentally (Figure 14).
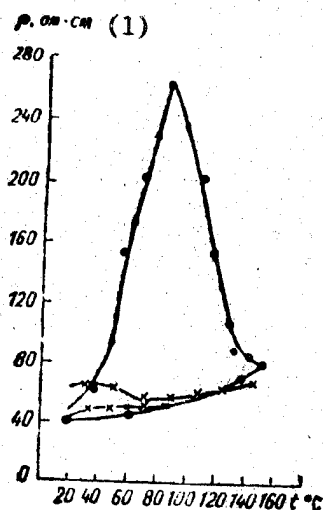

Figure 13. The specific resistance of the composition based on furfurolacetone monomer (with 50 percent carbon black) as a function of the test temperature. The consolidation temperature was 30 decrees C.
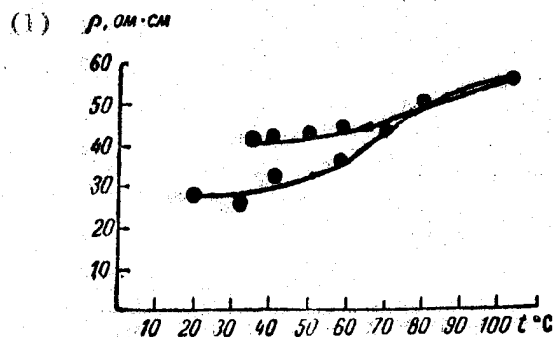
Key: 1. p, ohms·cm

Figure 14. The specific resistance of the composition based on furfurolacetone monomer (with 50 percent carbon black) as a function of the test temperature. The consolidation temperature was 80 degrees C.
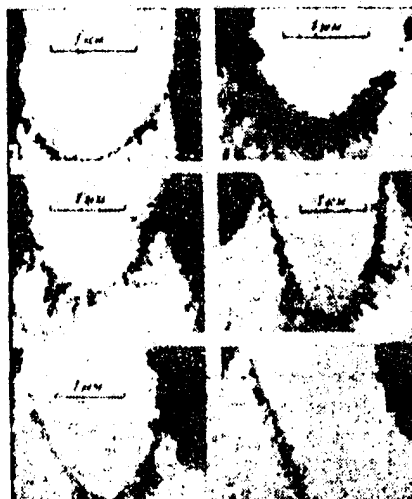
Key: 1. P, ohms·cm

Figure 15. Types of bridges formed on passage of a direct
current through an aluminum suspension in gasoline.

It should be noted that increasing the consolidation temperature
does not change the nature of the dependence of the resistance on the
carbon black content, but the resistances under other equal conditions
turn out to be less, which agrees with the concept of increasing the
number of carbon black-carbon black contents during volumetric shrinkage
of the material.

Thus, introduction of acetylene carbon black into the compositions
based on thermally reactive resins in order to increase their conductiv-
ity is accompanied by an essential change in consolidation time and
mechanical properties of the material.

The consolidation process connected with the formation and develop-
ment of the three-dimensional structure of the polymer is accompanied by
dispersion of the carbon black particles, and with known concentrations,
it is accompanied by the formation of chain conducting structures from them. In
order to create conducting structures of the filler, the defining factors
are the nature of interaction of the carbon black with the resin, the
tendency of the carbon black to form chain structures and a   quite high
actual concentration of carbon black particles.

Depending on the consolidation conditions the temperature coeffi-
cient of resistance has its own sign with higher or lower temperature
which is connected with shrinkage which occurs in this case. The local
superheating caused by the high current strength leads to destruction of
the conducting structures and to corresponding deviation of the relation
$J = f(V)$ from Ohm's law.

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Thus, it has been established that the conductivity of vulcanized rubbers and other polymer materials filled with carbon blacks is caused by the formation of chain structures from the carbon black particles. The carbon black aggregates connected to each other, or possibly separated by a thin film of binder, form conducting paths. The greater these paths in the sample cross section, the greater the conductivity. The same spatial conducting chain structures are also formed from metal particles in polymer compositions filled with metal powder. This determines their high conductivity. However, the formation of conducting three-dimensional metal structures is possible only for high concentrations of metal filler (400-500 parts by weight per 100 parts by weight of polymer binder). This leads to lowering of the physical and mechanical properties of the polymer material, a decrease in its strength and elasticity. Therefore, it has become necessary to develop procedures for artificial formation of conducting chains from particles of metal filler in a polymer material, permitting us to obtain high conductivity of the given polymer material with appreciably lower concentrations of metal filler.

One of these procedures is the formation of conducting structures in the polymer material under the effect of an electric field. Metal bridges have been detected and investigated in detail which resemble to a great extent carbon black chains occurring in suspensions of metals under the effect of an electric field (Figure 15). Recently L. G. Gindin, V. Ye. Gul', et al., [30,31] demonstrated that analogous structures occur under the effect of an electric field and in polymer materials filled with metals.

Another procedure for forming conducting chain structures in the polymer material is based on orientation and shift of the particles of metal ferromagnetic filler along the magnetic field force lines and subsequent consolidation of the filled polymer material in order to fix the metal chains formed. In Figure 16 we have the device for obtaining conducting materials in a magnetic field.

As a result of all these papers anisotropic conducting polymer materials with a specific volumetric electrical resistance of $\rho = 1 \cdot 10^{-2}$ ohms·cm along the metal chains formed are obtained with a concentration of metal filler of only 10-20 parts by weight per 100 parts by weight of polymer binder. In this case the mechanical strength of the polymer materials not only does not drop but even increases somewhat. Inasmuch as the indicated anisotropic conducting polymer materials are of significant practical interest, the necessity has arisen for more detailed investigation of the factors determining their conductivity.

V. Ye. Gul' and M. G. Golubeva [33] have established the quantitative dependence of the specific volumetric resistance of a polymer material filled with a disperse ferromagnetic filler on the magnetic field intensity. This relation has the following form:

$$\rho = AH^{-x},\qquad\qquad(2)$$

where A is the specific resistance of the system for H = 1 oersted or the oersted resistance of the system;

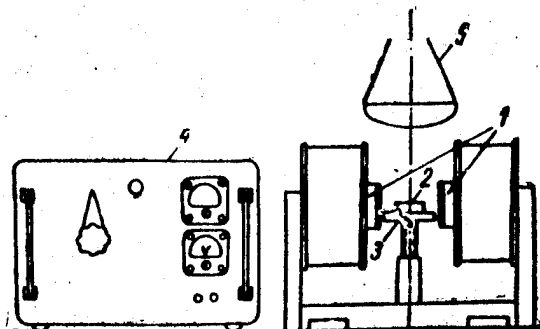K is the sensitivity of the specific resistance of the system to the magnetic field or the resistance sensitivity.

Figure 16. General view of the device for obtaining aniso- tropic conducting structures: 1--poles of the electromagnet; 2--tested sample; 3--stage; 4--AC rectifier; 5--infrared lamp.

It has been demonstrated that for unconsolidated compositions, K as a function of the intervals of H used has two values: K_1 and K_2 are the regions of low and high magnetic field intensities, respectively. The resistance sensitivity K is determined by the number of conducting chain structures formed per cm^3 of polymer material under the effect of the magnetic field and their conductivity. The dependence of the re- sistance sensitivity on temperature have been established. It is described by the two equations:

$$K = a\left(\frac{1}{T} - \frac{1}{T_k}\right);\qquad\qquad(3)$$

$$K = a\frac{1}{T} + K_{T\to\infty},\qquad\qquad(4)$$

where a is the angular temperature coefficient;

T_k is the temperature at which the system loses sensitivity to the magnetic field;

$K_{T\to\infty}$ is the resistance sensitivity of the system for an infinitely high temperature which would occur if the temperature increase were not accompanied by development of chemical processes.

The first equation is valid for systems containing low-conducting (ρ = 0.034-0.090 ohms·cm) ferromagnetic powders with $d_{ave} \leq 20$ microns and with $d_{ave} > 20$ microns at a concentration $C \leq 50$ parts by weight.

The second equation is characteristic for systems containing high-conducting (ρ = 0.001 ohms·cm) ferromagnetic powders with $d_{ave} > 20$ microns. The dependence of the parameters a, $K_{T \to \infty}$, $1/T_K$ on the average particle diameter d_{ave} and the weight concentration of the filler has been established. It has been demonstrated that the specific volumetric resistance of conducting polymer compositions filled with ferromagnetic metal powders and consolidated in a magnetic field is determined first of all by the magnitude of the transient contact resistances.

In a real system the particles of filler are not identical in size and shape (Figures 17,a and 17,b). With orientation in a magnetic field the filler particles are joined together not only at the ends but also by the lateral surfaces forming lattice structures along with elongated chains. The resistance of conducting chains made of individual metal particles depends on the contact area between these particles and the contact pressure [32]. Another mechanism of conductivity not subject to Ohm's law is also possible.

Figure 17,a. Microphotograph of nickel particles forming a conducting chain.

Figure 17,b. Microphotograph of nickel particles forming a conducting chain.

It was of interest to estimate the effect of the numerated factors on the resistance of the investigated systems. For this purpose the calculated and experimental values of ρ_V were compared for the epoxy resin filled with nickel powder with d_{ave} = 0.005 cm and consolidated in a magnetic field. From this comparison it follows that one of the

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effective means of lowering the resistance of the investigated systems
is decreasing the contact resistance between the particles.

As a result of the work which has been done in investigating laws
determining the properties of conducting polymer materials, conducting
polymer materials have been obtained not only under laboratory conditions
but also on an industrial scale. In this way, for example, the techno-
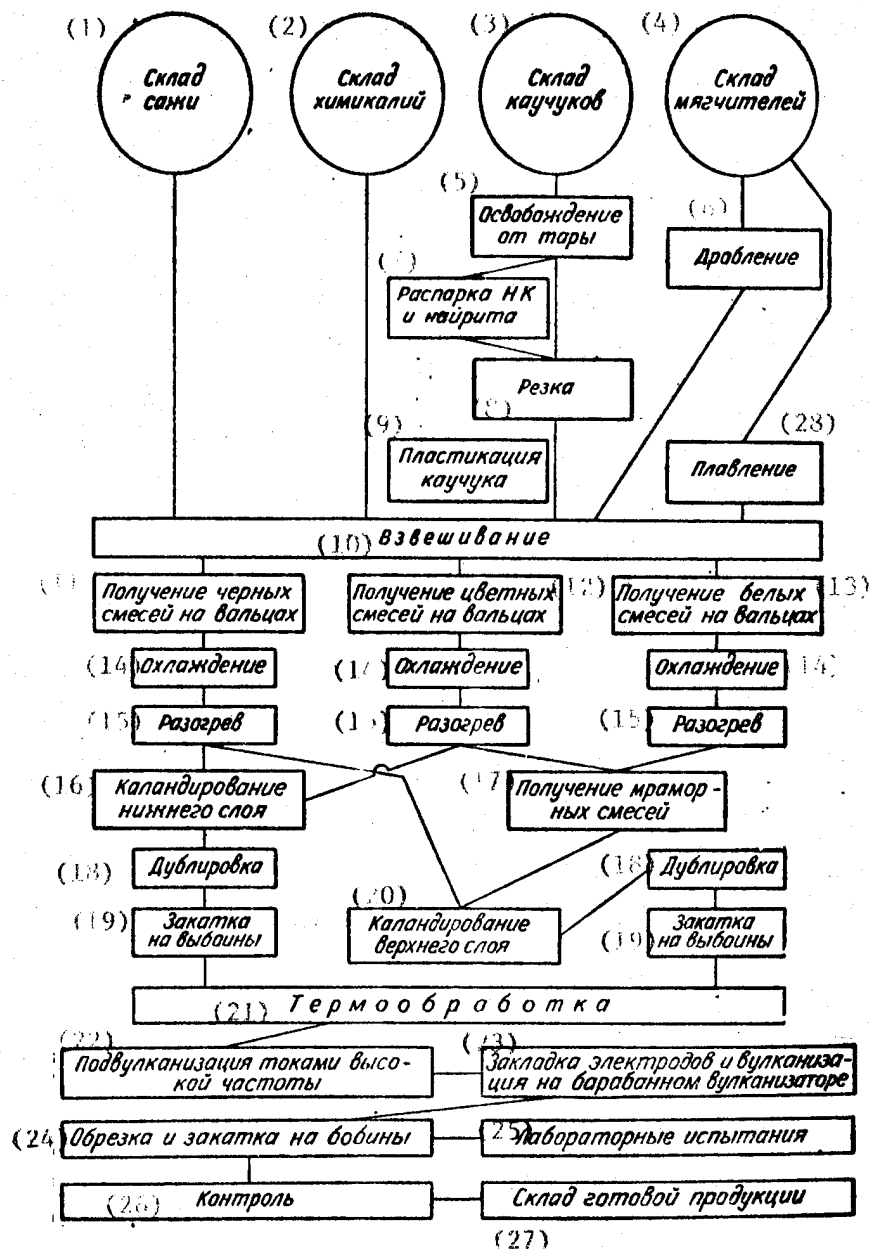logical process of manufacturing conducting rubbers has been developed.

Figure 18. Flow chart for the production of electric
            heating elements. (See key on next page).

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Key (to Figure 18, on preceding page):

1. carbon black storehouse
2. chemicals storehouse
3. rubber storehouse
4. mollifier storehouse
5. removal of packaging
6. crushing
7. softening of natural rubber and Nairit
8. cutting
9. plasticizing caoutchouc
10. weighing
11. obtaining black mixtures on rolls
12. obtaining colored mixtures on rolls
13. obtaining white mixtures on rolls
14. cooling
15. heating
16. calendering the lower layer
17. obtaining marble mixtures
18. doubling
19. rolling on rolls
20. calendering the upper layer
21. heat treatment
22. subvulcanization with high-frequency current
23. wrapping the electrodes and vulcanization on a drum vulcanizer
24. cutting and rolling on bobbins
25. laboratory testing
26. control
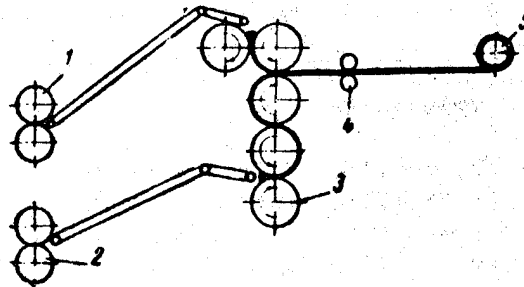27. storage for the finished product
28. melting

Figure 19. Feed, calendering and doubling schematic: 1--
feed rolls for insulating rubber; 2--feed rolls for conduct-
ing rubber; 3--five-roll calender; 4--doubling rolls; 5--
rolling unit.

In Figure 18 we have the flow chart for the production of electrical heating elements, and in Figures 19 and 20, the schematic of doubling and vulcanizing the heating elements made of conducting rubbers [1].

The heating element is manufactured as a whole from polymer mate-rials using, in addition to polymers, only thin metal electrodes for leading in the electric current.
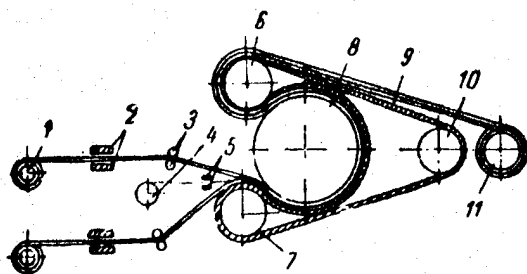
Figure 20. Vulcanization scheme: 1--rolling unit; 2--
heating unit; 3--rolls; 4--electrode rolling; 5--guide
plank; 6--drive drum: 7--pressing tape; 8--tension drum;
9--rolling.

The low temperature electric heating elements are sheets 0.7
meters wide and 3 mm thick. The length can be different. In particular,
the element can be made in the form of a band about 30 m long and rolled
with transporting into rolls. Each such sheet consists of three layers.

The middle layer is rubber made of natural or synthetic caoutchouc
containing about 80 percent special carbon black. This layer 2 mm thick
conducts an electric current and has a resistance on the order of 20-30
ohms·cm. Metal electrodes are molded in it at a spacing of 20 cm in the
form of strips   15-20 mm wide and 0.3 mm thick. The two outer layers
are insulating layers. They are also made of vulcanized natural or
synthetic rubber.

The heating elements can be considered as applied to direct and
alternating current at a voltage of 36, 127 and 220 volts. The input
depends on the dimensions of the heating surface of the element.

* * *

Thus, the scientific aspects of creating conducting polymer
materials, the technology for refining them and applications in various
branches of the national economy have been investigated in a highly
compressed form. Summing up, we probably are correct in concluding that
the work in the field of studying conductivity and creating new conduct-
ing materials is highly urgent for the national economy and undoubtedly
of interest in scientific respects.

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